

ZINC ALUMINATE HAVING A HIGH SPECIFIC SURFACE AREA, ITS
PROCESS OF PREPARATION AND ITS USE IN THE TREATMENT OF
EXHAUST GASES OF MOTOR VEHICLES

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The present invention relates to a zinc aluminate which is characterized in that it has, after being calcined at 800°C for 8 hours, a specific surface area of at least 85 m²/g. The invention also relates to a precursor composition for this aluminate. The process for the preparation of the aluminate and of the composition comprises the following steps: a zinc salt, sol or alkoxide and an aluminium alkoxide are brought together in a solvent medium; the mixture thus formed is hydrolysed by adding water in an excess amount with respect to the aluminium alkoxide; the precipitate formed is recovered and optionally dried, thereby obtaining the precursor composition; if required, the said precipitate is calcined, thereby obtaining the aluminate. Finally, the invention relates to the use of the aluminate in a process for treating exhaust gases of motor vehicles.

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The present invention relates to a zinc
10 aluminate having a high specific surface area, to a precursor composition for this aluminate, to a process for the preparation of this aluminate and of this composition, and to the use of the aluminate in a process for treating gases, especially exhaust gases of motor
15 vehicles.

It is known that the reduction of emissions of nitrogen oxides (NO_x) from the exhaust gases of motor-vehicle engines or of industrial plants constitutes a major environmental protection problem. In the case of
20 motor vehicles, "three-way" catalysts are particularly employed, which catalysts use stoichiometrically the reducing gases present in the mixture. However, any excess oxygen results in a sudden deterioration in the performance of the catalyst.

25 However, some engines, such as diesel engines or petrol engines operating in lean burn mode, are sparing in terms of fuel but emit exhaust gases which permanently contain a large excess of oxygen, for example

at least 5%. A standard three-way catalyst is therefore of no effect on the NO_x emissions from these engines. Moreover, the tightening of the standards with regard to motor vehicle postcombustion, which now extend to these 5 types of engines, makes it absolutely essential to limit NO_x emissions.

For these engines, catalysts in spinel form, based on aluminium and zinc, have been proposed. However, 10 these catalysts must be further improved since they do not have very high specific surface areas at high temperature. Now, surface stability, i.e. the fact of being able to maintain a high surface area at high temperature, is one aspect likely to improve the performance of catalysts.

15 There is therefore a need for a spinel-type catalyst having a high specific surface area.

To this end, the zinc aluminate of the invention is characterized in that it has, after being calcined at 800°C for 8 hours, a specific surface area 20 of at least 85 m²/g.

The invention also relates to a precursor composition for a zinc aluminate, which composition is characterized in that it comprises compounds of zinc and of aluminium and in that it is capable of forming, after 25 being calcined, a zinc aluminate, this aluminate having, after being calcined at 800°C for 8 hours, a specific surface area of at least 85 m²/g.

Another subject of the invention is a process

for the preparation of an aluminate or of a composition of the type described above, which process is characterized in that it comprises the following steps:

- a zinc salt and an aluminium alkoxide are
5 brought together in a solvent medium;
- the mixture thus formed is hydrolysed by adding water in an excess amount with respect to the aluminium alkoxide;
- the precipitate formed is recovered and
10 optionally dried, thereby obtaining the precursor composition;
- if required, the said precipitate is calcined, thereby obtaining the aluminate.

Further characteristics, details and advantages
15 of the invention will become even more apparent on reading the description which follows, together with the various concrete but non-limiting examples intended to illustrate it.

The aluminate of the invention is a zinc
20 aluminate. It has a structure of the spinel type, $ZnAl_2O_4$. It may be in the form of one or more phases which are zinc-depleted or zinc-enriched with respect to $ZnAl_2O_4$, these phases satisfying the formulae $Zn_{1-x}Al_2O_{4-\delta}$ and $Zn_{1+x}Al_2O_{4+\delta}$, where $0 < x \leq 0.95$. The values of x may more
25 particularly satisfy the following relationships: $0 < x \leq 0.85$, $0 < x \leq 0.8$ and more particularly $0 < x \leq 0.5$. Finally, x may satisfy the relationship $0.4 \leq x \leq 0.85$. The aluminate may furthermore contain one

or more additives. These additives may be chosen from the elements of Groups IA, IIA, VIIA to IB of the Periodic Table and from tin, gallium and the rare earths.

The Periodic Table of the Elements to which reference is made is the one published in the Supplément au Bulletin de la Société Chimique de France (*Supplement to the Bulletin of the Chemical Society of France*) No. 1 (January 1966). Moreover, the term "rare earths" should be understood to mean the elements of the group formed by yttrium and the elements of the Periodic Table having an atomic number of between 57 and 71 inclusive.

As element of Group VIIA, mention may more particularly be made of manganese; as element of Group VIII, mention may especially be made of iron; as elements of Group IB, mention may more particularly be made of copper and silver.

These additives may especially be present in the aluminate as partial substitution for the zinc or for the aluminium.

One characteristic of the aluminate of the invention is its specific surface area. The term "specific surface area" should be understood to mean here, and for the rest of the description, the BET specific surface area determined by nitrogen adsorption in accordance with the ASTM D 3663-78 standard established from the Brunauer - Emmett - Teller method described in the publication "The Journal of the American Chemical Society, 60, 309 (1938)".

Even after being calcined at high temperature, the aluminate of the invention still has a high value of surface area. Thus, after calcining at 800°C for 8 hours, this specific surface area is at least 85 m²/g. It may be 5 at least 90 m²/g and more particularly at least 100 m²/g, still after calcining at 800°C for 8 hours. Values of at least 120 m²/g may be achieved.

High values of this surface area are maintained at even higher temperatures since the aluminate of the 10 invention may have, after being calcined at 900°C for 2 hours, a specific surface area of at least 70 m²/g, more particularly at least 80 m²/g. Furthermore, at 1000°C after calcining for 6 hours, specific surface areas of at least 50 m²/g, more particularly at least 70 m²/g may be 15 observed. This means that the surface area of the aluminate is stable over a wide temperature range. The values which have just been given above extend to calcining in air. In addition, it may be noted that the aluminate of the invention has a high ageing resistance. 20 What is meant by this is that, under particular calcining conditions, its specific surface area varies relatively little. Thus, after calcining for 6 hours at 1000°C in an H₂O/N₂ medium with 10% H₂O by volume, the surface area remains substantially the same as that obtained after 25 calcining in air at the same temperature and for the same duration, namely at least 50 m²/g. The same results are obtained for calcining in an O₂/H₂O/N₂ medium with 10% H₂O and 10% O₂ by volume.

Moreover, the aluminate of the invention may have a pore volume of at least 0.6 ml/g, this porosity being determined by mercury intrusion porosimetry. The measurements were made using a Micromeretics Auto Pore 5 9220 machine on powders degassed overnight in an oven heated at 200°C. The operating parameters are as follows: penetrometer constant : 21.63, capillary volume : 1.1, contact angle : 140°. The porosity may more particularly be at least 2 ml/g and may be, for example, between 2.5 10 and 3.5 ml/g.

The invention also relates to a precursor composition for the aluminate, such as the one that has just been described above.

This composition comprises compounds of zinc 15 and of aluminium and, if required, compounds of the abovementioned additives. The main characteristic of the precursor composition is its ability, after being calcined, to give a zinc aluminate. The calcining temperature above which the aluminate forms is 20 approximately 500°C. Furthermore, the aluminate thus obtained has the characteristics given above, that is to say that, if it is calcined at a temperature of 800°C for 8 hours, it retains a high specific surface area of at least 85 m²/g, more particularly at least 90 m²/g and even 25 more particularly at least 100 m²/g. Of course, all the surface area values given above with regard to the aluminate at temperatures of 800°C and 900°C also apply here.

The process for the preparation of the aluminate and of its precursor composition will now be described.

The first step of this process consists in
5 bringing a zinc salt, sol or alkoxide and an aluminium alkoxide together in a solvent medium, optionally with a salt, sol or alkoxide of at least one aforementioned additive. The zinc salt or alkoxide, as well as the salt or alkoxide of the additive, must be soluble in the
10 solvent medium. The zinc salt or the salt of the additive is, for example, an inorganic salt such as a nitrate or a chloride or else an organic salt such as a citrate, an oxalate or an acetate. The aluminium alkoxide may, for example, be an ethoxide, a butoxide or an isopropoxide.
15

The solvent medium is chosen from any medium in which the zinc salt or alkoxide and the aluminium alkoxide are soluble. Generally, an alcoholic solvent is used. As alcoholic solvent, mention may be made of saturated monoalcohols and more particularly those having a short chain (for example at most C₈), such as methanol, ethanol, propanol and butanol. It is also possible to use unsaturated alcohols and polyalcohols, such as, for example, ethylene glycol, propylene glycol, hexylene glycol, propanediol and butanediol. A ketone such as
20 acetylacetone may also be used.
25

The reactants may be brought together in the solvent medium in any manner. However, according to one particular embodiment of the invention, the zinc salt and

the aluminium alkoxide are brought together by adding to the aluminium alkoxide, which constitutes a stock, the zinc salt in the solvent medium, i.e. dissolved beforehand in this medium.

5 It will be noted here, according to another version of the invention, that it is possible to heat the mixture thus obtained. This makes it easier for the salts to dissolve and allows the next step - hydrolysis and precipitation - to be better controlled.

10 The second step of the process of the invention consists in hydrolysing the mixture obtained from the previous step.

15 This hydrolysis takes place by adding water to the mixture. According to one characteristic of the process of the invention, the hydrolysis is carried out by using an excess amount of water with respect to the aluminium alkoxide. This excess is determined by the H_2O /aluminium alkoxide molar ratio. In general, this ratio may be at least 6, more particularly at least 10 and even 20 more particularly at least 20. However, in the case of the preparation of a zinc-depleted aluminate, this ratio may be lower. More specifically, in the case of the preparation of an aluminate having a Zn/Al ratio of less than 0.4, the H_2O /aluminium alkoxide molar ratio may be at least 3, more particularly at least 4.

25 The water may be provided in the form of a water-alcohol mixture, it being possible for the alcohol to be especially chosen from those mentioned above with

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regard to the solvent medium. Mention may more particularly be made of ethanol.

The hydrolysis results in the formation of a precipitate of the elements.

5 The precipitate obtained is separated from the reaction mixture by any known means, especially by centrifuging.

If necessary, the precipitate may be washed.

Optionally, the precipitate may then be dried.

10 At this stage, the precursor composition of the invention is obtained. The aluminate is prepared by calcining the precipitate (precursor composition) at a temperature of at least 500°C.

Mention may be made of another process for the preparation of an aluminate or of a precursor according to the invention if this aluminate or precursor comprises an additive of the type mentioned above. This process consists in adding the additive not during the synthesis of the aluminate but by impregnating either the precursor composition, for example the dried precipitate, or the aluminate itself, i.e. the calcined precipitate. The impregnation is carried out using a solution of a salt of the additive of the type given above for example.

25 Dry impregnation is more particularly used. Dry impregnation consists in adding to the product to be impregnated a volume of an aqueous solution of the element which is equal to the pore volume of the solid to be impregnated.

Moreover, the invention relates to a process for the treatment of exhaust gases of motor vehicles, in which a catalytic system comprising an aluminate as described above is used.

5 The invention also relates to a process in which a catalytic system comprising this same aluminate is used for the treatment of gases which may comprise nitrogen oxides for the purpose of reducing the emissions of these nitrogen oxides.

10 In this case, the gases capable of being treated are, for example, those coming from gas turbines, from boilers of thermal power stations or else from internal combustion engines. In the latter case, these may be especially diesel engines or engines operating in 15 lean burn mode.

The aluminate of the invention thus applies to the treatment of gases having a high oxygen content and containing nitrogen oxides, for the purpose of reducing the emissions of these oxides. The expression "gases 20 having a high oxygen content" should be understood to mean gases having an excess of oxygen with respect to the amount necessary for stoichiometric combustion of the fuels and, more particularly, gases permanently having an excess of oxygen with respect to the stoichiometric value 25 $\lambda = 1$. The value λ is correlated to the air/fuel ratio in a manner known per se, especially a manner known in the field of internal combustion engines. In other words, the aluminate of the invention applies to the treatment of

gases coming from systems of the type described in the previous paragraph and operating permanently under conditions such that λ is always strictly greater than 1. In the case of gases having a high oxygen content, the 5 aluminate of the invention thus applies, on the one hand, to the treatment of the gases from an engine which is operating in lean burn mode and which has a high oxygen content (expressed by volume) of generally between 2.5 and 5% and, on the other hand, to the treatment of gases 10 which have an even higher oxygen content, for example the gases from diesel-type engines, i.e. at least 5% or more than 5%, more particularly at least 10%, it being possible, for example, for this content to be between 5 and 20%.

15 The gases contain a reducing agent which may be one or more hydrocarbons and one of the reactions that it is desired to catalyse in this case is the HC (hydrocarbons) + NO_x reaction.

20 The hydrocarbons which may be used as reducing agent for eliminating the NO_x are especially gases or liquids from the families of saturated carbides, ethylenic carbides, acetylenic carbides, aromatic carbides and hydrocarbons of petroleum cuts such as, for example, methane, ethane, propane, butane, pentane, 25 hexane, ethylene, propylene, acetylene, butadiene, benzene, toluene, xylene, kerosene and gas oil.

The gases may also contain, as reducing agent, organic compounds containing oxygen. These compounds may

especially be alcohols, for example of the saturated alcohol type, such as methanol, ethanol or propanol; ethers such as methyl ether or ethyl ether; esters such as methyl acetate and ketones.

5 The gases may also contain ammonia as a reducing agent.

In this application to the treatment of gases, the aluminate may be used in catalytic compositions which may be in various forms, such as granules, beads, 10 cylinders or a honeycomb of varying dimensions, it being possible for these compositions to comprise the aluminate of the invention on any support normally used in the field of catalysis, such as, for example, ZrO_2 , Al_2O_3 , TiO_2 , CeO_2 , SiO_2 or mixtures thereof.

15 The invention also relates more particularly to a catalytic system for the gas treatment processes described above. This system is characterized in that it comprises an aluminate on a substrate. Such a system generally comprises a wash coat incorporating the 20 aluminate and a support of the type described above, the wash coat being deposited on a substrate, for example a substrate of the metal or ceramic monolith type.

The systems are mounted in a known manner in the exhaust pipes of vehicles in the case of the 25 application to the treatment of exhaust gases.

Finally, the invention also relates to the use of an aluminate or of a precursor composition, such as those described above, for the manufacture of such a

catalytic system. Examples will now be given.

EXAMPLE 1

This example relates to the preparation of
5 ZnAl_2O_4 .

The following raw materials are used:

- Crystallized 99% pure $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, molecular weight: 297.47
10 - 97% pure aluminium tri-sec-butoxide
 $(\text{C}_2\text{H}_5\text{CH}_2\text{CH}_2\text{O})_3\text{Al}$
- 99% pure hexylene glycol (2-methyl 2,4-pentanediol)
- absolute ethanol, molecular weight: 46.07; $d: 0.79 \text{ g/cm}^3$.

15 1.25 mol of the zinc salt are dissolved in 1 l of hexylene glycol. This solution is added to 2.5 mol of aluminium tri-sec-butoxide introduced beforehand into the reactor, in a single go and with vigorous stirring (500 rpm). The mixture is heated up to 70°C and kept at 20 this temperature for 2 hours. Next, a water/ethanol (50/50 by volume) mixture is added at a rate of 5 ml/minute. The water/aluminium tri-sec-butoxide ratio is equal to 28. The mixture is left to cool overnight with stirring. The precipitate obtained is separated by 25 centrifuging. The precipitate is oven-dried as a thin layer at 70°C for 48 h. Finally, the product is calcined. The temperature rise is 5°C/minute. Next, the temperature is maintained at a constant level with the value given

above and for the times given above.

After calcining for 6 hours at 600°C, the specific surface area of the product is 136 m²/g.

5 After calcining for 6 hours at 700°C, the specific surface area of the product is 125 m²/g.

After calcining for 8 hours at 800°C, the specific surface area of the product is 115 m²/g.

After calcining for 2 hours at 900°C, the specific surface area of the product is 101 m²/g.

10 After calcining for 2 hours at 1000°C, the specific surface area of the product is 76 m²/g and it is 53 m²/g after 6 hours at the same temperature.

15 After calcining for 6 hours at 1000°C in an H₂O/N₂ mixture with 10% H₂O by volume, the surface area remains equal to 53 m²/g. The same result is obtained for calcining for 6 hours at 1000°C in an O₂/H₂O/N₂ medium with 10% H₂O and 10% O₂ by volume.

EXAMPLE 2

20 The precipitate obtained in Example 1 is dried for 48 h at 70°C. Next, it is impregnated with a solution of SnCl₂·2H₂O dissolved in ethanol. The technique used is dry impregnation. The amount of Sn deposited is equal to 1.6% by weight with respect to the zinc aluminate oxide. 25 The product thus obtained is oven-dried for 2 h at 110°C and then calcined for 8 h at 800°C (rate of rise, 5°C/minute).

The specific surface area of the product thus

obtained is equal to 115 m²/g.

EXAMPLE 3

This example relates to the preparation of
5 ZnAl_{1.8}Ga_{0.2}O₄.

The same raw materials as in Example 1 are used with, in addition, a 1.807 mol/l solution of Ga(NO₃)₃, d = 1.365 g/cm³.

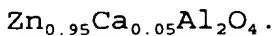
1.25 mol of the zinc salt are dissolved in
10 1 litre of hexylene glycol into which 0.25 mol of gallium nitrate is then introduced.

This solution is added to 2.25 mol of aluminium tri-sec-butoxide introduced beforehand into the reactor, with vigorous stirring (500 rpm). The mixture is heated
15 to 70°C and maintained at this temperature for 2 hours. A water/ethanol (50/50 by volume) mixture is then added at a rate of 5 ml/minute. The water/aluminium tri-sec-butoxide ratio is equal to 25. The mixture is left to cool overnight with stirring. The precipitate
20 obtained is separated by centrifuging. The precipitate obtained is dried as a thin layer at 70°C for 48 h and then calcined for 8 hours at 800°C (rate of rise 5°C/minute).

The specific surface area of the product thus
25 obtained is equal to 113 m²/g.

EXAMPLE 4

This example relates to the preparation of



The same raw materials as in Example 1 are used with, in addition, a solution of 98% pure $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$.

1.19 mol of the zinc salt are dissolved in 5 1 litre of hexylene glycol into which 0.06 mol of calcium nitrate is then introduced.

This solution is added to 2.5 mol of aluminium tri-sec-butoxide introduced beforehand into the reactor, with vigorous stirring (500 rpm). The mixture is heated 10 to 70°C and maintained at this temperature for 2 hours. A water/ethanol (50/50 by volume) mixture is then added at a rate of 5 ml/minute. The water/aluminium tri-sec-butoxide ratio is equal to 28. The mixture is left to cool overnight with stirring. The precipitate 15 obtained is separated by centrifuging. The precipitate obtained is dried as a thin layer at 70°C for 48 h and then calcined for 8 hours at 800°C (rate of rise 5°C/minute).

The specific surface area of the product thus 20 obtained is equal to 119 m^2/g .

EXAMPLE 5

This example relates to the preparation of $\text{Zn}_{0.95}\text{Li}_{0.05}\text{Al}_2\text{O}_4$.

25 The same raw materials as in Example 1 are used with, in addition, a solution of 99% pure $\text{Li}(\text{NO}_3)_2$.

1.19 mol of the zinc salt are dissolved in 1 litre of hexylene glycol into which 0.06 mol of lithium

nitrate is then introduced.

This solution is added to 2.5 mol of aluminium tri-sec-butoxide introduced beforehand into the reactor, with vigorous stirring (500 rpm). The mixture is heated 5 to 70°C and maintained at this temperature for 2 hours. A water/ethanol (50/50 by volume) mixture is then added at a rate of 5 ml/minute. The water/aluminium tri-sec-butoxide ratio is equal to 28. The mixture is left to cool overnight with stirring. The precipitate 10 obtained is separated by centrifuging. The precipitate obtained is dried as a thin layer at 70°C for 48 h and then calcined for 8 hours at 800°C (rate of rise 5°C/minute).

The specific surface area of the product thus 15 obtained is equal to 108 m²/g.

EXAMPLE 6

This example relates to an aluminate of formula ZnAl₂O₄ which comprises silver as additive.

20 The precipitate obtained in Example 1 is dried for 48 h at 70°C. Next, it is impregnated with a solution of AgNO₃ (99.8%). The technique used is dry impregnation. The amount of silver deposited is equal to 1.6% by weight with respect to the zinc aluminate oxide. The product 25 thus obtained is oven dried for 2 h at 110°C and then calcined for 8 h at 800°C (rate of rise 5°C/minute).

The specific surface area of the product thus obtained is equal to 90 m²/g.

EXAMPLE 7

The process as in Example 1 is carried out in order to prepare zinc aluminates having different Zn/Al ratios. The same raw materials are used, in the necessary proportions. For the products 7-1 to 7-3, the H₂O/aluminium alkoxide molar ratio is 28. For the products 7-4 to 7-6, this ratio is 4. The characteristics of the products prepared are given below.

10	Products	Formulae	Specific surface area
			(8 h at 800°C) in m ² /g
	7-1	Zn _{1.05} Al ₂ O ₄	88
	7-2	Zn _{0.95} Al ₂ O ₄	92
15	7-3	Zn _{0.8} Al ₂ O ₄	140
	7-4	Zn _{0.6} Al ₂ O ₄	102
	7-5	Zn _{0.4} Al ₂ O ₄	139
	7-6	Zn _{0.3} Al ₂ O ₄	110

EXAMPLE 8

In this example, the products obtained in the previous examples are tested in order to evaluate their catalytic performance.

A quartz reactor is charged with 0.2 g of the catalyst powder. The powder used was precompacted and then ground and screened so as to isolate the particle size range between 0.125 and 0.250 mm.

The reaction mixture entering the reactor has the following composition (by volume) :

- NO = 300 ppmv
- C₃H₆ = 150 ppmv or 450 ppmv
- C₃H₈ = 150 ppmv or 450 ppmv
- CO = 350 ppmv

5

- O₂ = 10%
- CO₂ = 10%
- H₂O = 10%
- N₂ = qsp 100%

The overall flow rate is 30 Nl/h.

10 The HSV is about 200,000 h⁻¹.

The HC(C₃H₆ + C₃H₈), NO and NO_x (NO_x = NO + NO₂) signals are continuously recorded, as is the temperature in the reactor.

15 The HC signal is given by a total HC Beckman detector based on the principle of detection using flame ionization.

20 The NO and NO_x signals are given by an Ecophysics NO_x analyser based on the principle of chemiluminescence: it gives the NO, NO_x and NO₂ values, the latter being calculated from the difference between the NO_x and NO signals.

25 The catalytic activity is measured from the HC, NO and NO_x signals as a function of temperature during a programmed temperature rise of 150 to 700°C at a rate of 15°C/minute and from the following equations:

- The degree of conversion of NO (TNO) in %, which is given by:

$$TNO = 100 (NO^0 - NO) NO^0$$

where NO^0 is the NO signal at the time $t = 0$, which corresponds to the NO signal obtained with the reaction mixture by-passing the catalytic reactor and NO is the NO signal at the time t .

5 - The degree of conversion of HC (THC) in %, which is given by:

$$THC = 100(HC^0 - HC)/HC^0$$

where HC^0 is the HC signal at the time $t = 0$, which corresponds to the HC signal obtained with the reaction 10 mixture by-passing the catalytic reactor and HC is the HC signal at the time t .

- The degree of conversion of NO_x (TNO_x) in %, which is given by:

$$TNO_x = 100(NO_x^0 - NO_x)/NO_x^0$$

15 where NO_x^0 is the NO_x signal at the time $t = 0$, which corresponds to the NO_x signal obtained with the reaction mixture by-passing the catalytic reactor and NO_x is the NO_x signal at the time t .

Table 1 below gives the results obtained with the product of Example 1 calcined for 8 h at 800°C and for a reaction mixture in which NO = 300 ppmv, 5 C₃H₆ = C₃H₈ = 150 ppmv, i.e. an HC₁/NO ratio of 3 (HC₁ being expressed as the carbon number, i.e. here 6 x 150/300).

Table 1

Temperature (°C)	THC (%)	TNO (%)	TNO _x (%)
350	0.6	1.1	1.3
400	1	2.1	2
450	6	8.8	7.9
500	24.8	23.3	23.7
550	46.4	44.5	44.3
600	75.6	59.5	59.4
650	99	28	25.8

Table 2 below gives the results obtained with the product of Example 1 calcined for 8 h at 800°C, for a reaction mixture in which NO = 300 ppmv,
 5 C₃H₆ = C₃H₈ = 450 ppmv, i.e. an HC₁/NO ratio of 9.

Table 2

	Temperature (°C)	THC (%)	TNO (%)	TNO _x (%)
10	350	0.8	0.2	1.4
15	400	1.8	0	1.4
	450	7.5	4.8	6.2
	500	29	32.1	32.8
	550	50.9	71.5	70.9
	600	71.9	87.9	86.4
	650	95	69	63.9

Table 3 below gives the results obtained with the product of Example 1 calcined for 2 h at 900°C and for the same reaction mixture as in Example 1, i.e. an HC₁/NO ratio of 3.

Table 3

Temperature (°C)	THC (%)	TNO (%)	TNO _x (%)
350	0.3	0	0
400	0.7	0	0
450	2.1	1.2	2
500	10.5	11	11.3
550	3.1	28.2	28.5
600	68.6	52.6	52.9
650	97.9	28.7	27.5

Table 4 below gives the results obtained with the product of Example 1 calcined for 2 h at 1000°C and for the same reaction mixture as in Example 1, i.e. an HC₁/NO ratio of 3.

Table 4

Temperature (°C)	THC (%)	TNO (%)	TNO _x (%)
350	0	0	0
400	0	0	0
450	1.3	1.5	1.2
500	9.4	12.5	12.2
550	34.1	37.6	37.5
600	80.9	51.7	51.2
650	100	21.5	18.3

Table 5 below gives the results obtained with the product of Example 2 calcined for 2 h at 800°C and for the same reaction mixture as in the first case of the 5 product of Example 1, i.e. an HC₁/NO ratio of 3.

Table 5

Temperature (°C)	THC (%)	TNO (%)	TNO _x (%)
350	0	2.2	2.6
400	0.9	3.3	3.7
450	5.6	10.9	11.2
500	25	32	32.2
550	49	38.4	38.1
600	63.3	31.1	28.6
650	87.4	26.8	21.2

Table 6 below gives the results obtained with the product of Example 2 calcined for 2 h at 800°C for a reaction mixture in which NO = 300 ppmv,
 5 C₃H₆ = C₃H₈ = 450 ppmv, i.e. an HC₁/NO ratio of 9.

Table 6

Temperature (°C)	THC (%)	TNO (%)	TNO _x (%)
350	2.6	1.3	1.3
400	6.1	3.8	3.2
450	13.9	12.5	12.4
500	35.1	47.3	47.3
550	55.4	54.4	54.1
600	71.8	42	41.7
650	96.7	31.9	29.8

Table 7 below gives the results obtained with the product of Example 7 calcined for 2 h at 800°C and for a reaction mixture with an HC₁/NO ratio of 3. Furthermore, 5 the product is used in an amount of 100 mg of powder with 100 mg of SiC.

Table 7

Temperature (°C)	THC (%)	TNO (%)	TNO _x (%)
350	2.6	2.1	2.6
400	2.9	1.4	2.1
450	4.8	4.2	4.2
500	21.1	26.6	26.2
550	63	46.4	45
600	90	34.5	30.1
650	98.9	24.5	7

Table 8 below gives the maximum % NO_x values obtained, and the corresponding temperature, with products of Example 8 that are calcined for 2 h at 800°C and for a reaction mixture having an HC₁/NO ratio of 3. Furthermore, the products are used in an amount of 100 mg of powder with 100 mg of SiC.

Table 8

10

15

Products	% NO _x and temperature
7-3	35% 620°C
7-4	38% 625°C
7-5	42% 600°C
7-6	46% 600°C